Standard Operating Procedure for the Analysis of Metals in Waters and Wastewaters by ICP Method 200.7 Using the Perkin Elmer Optima 3300 DV and 4300 DV

LG213

Original, April 2004

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1.0 SCOPE AND APPLICATION

1.1 This Standard Operating Procedure (SOP) is applicable to the analyses of twenty-nine elements in waters and wastewaters using CRL digestion procedure METALS025 (200.2 Hotblock method). The analysis method is based on 200.7 which is approved for NPDES monitoring in 40 CFR part 136.3, Table 1B for 25 of these elements. Twelve of these are priority pollutants per 40 CFR part 401.15. Of the 25, 21 of them are reported routinely by CRL, as well as three other unregulated elements. The other four may be reported if present in sufficient amount. Other subsets of these may be reported for various programs based on the Data Quality Objectives (DQOs) of the project. At the CRL, as a matter of routine, As, Se, Sb and Tl are reported by Graphite Furnace Atomic Absorption (GFAA). The sensitivity of this method allows these elements to be reported by ICP depending on the DQOs of the project, for example, for TCLPs

1.2 The instrument used for the analysis of metals by ICP as described here is the Perkin Elmer Optima 3300 DV or the 4300 DV, using both an axial and radial view of the plasma.

1.3 The method detection limits (μg/L), reporting levels (μg/L), limits of linearity (μg/L) and the plasma view for the 3300 DV are listed below:

Element/Wavelength	Method Detection Limit (μg/L)	Reporting Level (μg/L)	Linearity Limit (μg/L)	Plasma View
Ag 328.068	1.1	5.0	100	Axial
Ag 338.289	1.3	5.0	100	Axial
Al 308.215	32	100	1,000,000	Radial
Al 394.401	13	75	1,000,000	Radial
Al 396.153	14	50	1,000,000	Radial
As 188.979	7.2	30	100,000	Axial
As 193.696	11	30	100,000	Axial
As 197.197	420	1000	100,000	Radial
B 208.889	52	200	10,000	Radial
B 249.677	28	100	10,000	Radial
B 249.772	26	100	10,000	Radial
Ba 233.527	3.0	10	100,000	Radial
Ba 455.403	0.40	2.0	10,000	Radial
Ba 493.408	1.0	5.0	100,000	Radial
Be 234.861	0.3	1.0	10,000	Radial
Be 313.042	0.1	0.5	10,000	Axial
Be 313.107	0.3	1.0	10,000	Axial
Ca 315.887	13	50	500,000	Radial
Ca 317.933	13	50	100,000	Radial
Cd 214.440	0.4	2.0	30,000	Axial
Cd 226.502	0.5	2.0	30,000	Axial
Cd 228.802	5.2	20	100,000	Radial
Ce 413.380	15	50	100,000	Radial
Ce 413.764	12	50	100,000	Radial
Ce 418.660	9	50	100,000	Radial
Co 228.616	0.1	2.0	10,000	Axial

Element/Wavelength	Method Detection Limit (μg/L)	Reporting Level (μg/L)	Linearity Limit (μg/L)	Plasma View
Co 230.786	11	40	100,000	Radial
Co 238.892	0.3	2.0	100,000	Axial
Cr 205.560	24	100	100,000	Radial
Cr 267.716	0.6	3.0	30,000	Axial
Cr 283.563	1.3	5.0	100,000	Axial
Cu 224.700	32	100	1,000,000	Radial
Cu 324.752	0.7	4.0	100,000	Axial
Cu 327.393	0.7	4.0	100,000	Axial
Fe 238.204	6.3	20	10,000	Radial
Fe 239.562	11	40	10,000	Radial
Fe 259.939	6.1	20	10,000	Radial
Fe 273.955	11	40	100,000	Radial
K 766.490	130	800	700,000	Radial
Li 610.362	200	600	10,000	Radial
Li 670.784	4.0	25	10,000	Radial
Mg 279.077	29	100	1,000,000	Radial
Mg 280.271	5.7	20	10,000	Radial
Mg 285.213	7.6	40	10,000	Radial
Mn 257.610	0.50	2.0	100,000	Radial
Mn 259.372	1.1	4.0	100,000	Radial
Mn 260.568	1.3	4.0	100,000	Radial
Mo 202.031	2.2	10	100,000	Axial
Mo 203.845	210	1000	100,000	Radial
Mo 204.597	3.7	15	100,000	Axial
Na 588.995	190	500	100,000	Radial
Na 589.592	49	200	100,000	Radial
Ni 221.648	60	250	100,000	Radial
Ni 231.604	0.6	2.0	30,000	Axial
Ni 232.003	2.1	8.0	100,000	Axial
Pb 217.000	14	50	100,000	Axial
Pb 220.353	6.0	20	100,000	Axial
Sb 206.836	8	30	100,000	Axial
Sb 217.582	8.2	30	100,000	Axial
Se 196.026	16	50	100,000	Axial
Se 203.985	18	60	100,000	Axial
Sn 189.927	2.7	10	10,000	Axial
Sn 235.485	26	100	10,000	Axial
Sr 407.771	0.4	2.0	10,000	Radial
Sr 421.552	0.1	0.85	10,000	Radial
Sr 460.733	0.1	85	1,000,000	Radial
Ti 334.940	0.6	2.0	100,000	Radial
Ti 336.121	1.0	4.0	100,000	Radial
Ti 337.279	1.8	6.0	100,000	Radial
Tl 190.801	7.9	30	100,000	Axial
Tl 276.787	12	45	100,000	Axial
Tl 351.924	20	65	100,000	Axial
V 292.402	0.3	2.0	100,000	Axial
V 311.071	0.4	2.0	100,000	Axial
V 310.230	2.5	10	100,000	Radial
Zn 202.548	14	60	10,000	Radial
Zn 206.200	17	60	100,000	Radial

Element/Wavelength	Method Detection Limit (μg/L)	Reporting Level (μg/L)	Linearity Limit (μg/L)	Plasma View
Zn 213.857	7.2	30	10,000	Radial

1.4 The last date of verification of these MDLs was September 2003.

1.5 The method detection limits (μg/L), reporting levels (μg/L), limits of linearity (μg/L) and the plasma view for the 4300 DV are listed below (not all lines are included; only the primary lines for reporting are given):

Element/Wavelength	Method Detection Limit (μg/L)	Reporting Level (μg/L)	Linearity Limit (μg/L)	Plasma View
Ag 328.068	1.6	5.0	100	Axial
Ag 338.289	2.7	8.0	100	Axial
Al 308.215	19	100	1,000,000	Radial
Al 396.153	22	100	500,000	Radial
As 188.979	4.4	15	100,000	Axial
As 193.696	5.4	15	100,000	Axial
B 249.677	27	100	100,000	Radial
Ba 455.403	0.7	2.0	20,000	Radial
Be 313.042	0.2	1.0	10,000	Axial
Ca 315.887	14	60	1,000,000	Radial
Cd 214.440	0.2	1.0	20,000	Axial
Cd 226.502	0.3	1.0	100,000	Axial
Co 228.616	0.4	2.0	100,000	Axial
Cr 267.716	1.2	4.0	100,000	Axial
Cu 324.752	0.9	5.0	50,000	Axial
Cu 327.393	1.8	5.0	100,000	Axial
Fe 259.939	3.7	20	500,000	Radial
Fe 273.955	6.0	20	2,000,000	Radial
K 766.490	660	2,000	1,000,000	Radial
Li 670.784	5.1	25	100,000	Radial
Mg 279.077	8.6	40	1,000,000	Radial
Mg 280.271	5.0	20	10,000	Radial
Mn 257.610	0.3	1.0	50,000	Radial
Mo 202.031	1.0	4.0	100,000	Axial
Mo 204.597	1.4	4.0	100,000	Axial
Na 589.592	55	400	700,000	Radial
Ni 231.604	0.6	2.0	100,000	Axial
Pb 220.353	4.6	15	100,000	Axial
Sb 206.836	4.4	20	100,000	Axial
Se 196.026	7.0	30	100,000	Axial
Sn 189.927	2.0	10	100,000	Axial
Sr 407.771	0.2	1.0	10,000	Radial
Sr 421.552	0.4	1.0	20,000	Radial
Ti 334.940	1.3	5.0	100,000	Radial

Element/Wavelength	Method Detection Limit (μg/L)	Reporting Level (μg/L)	Linearity Limit (μg/L)	Plasma View
Ti 336.121	1.4	5.0	100,000	Radial
Tl 190.801	7.7	20	100,000	Axial
V 292.402	1.7	6.0	100,000	Axial
Zn 213.857	4.8	40	100,000	Radial

The date of verification of these MDLs was October 2003.

1.6 Samples with silver values greater than 0.1 mg/L in the digest will be diluted, redigested and reanalyzed, due to the relatively low HCl concentration in the 200.2 digestion.

1.7 If reporting between the MDL and the reporting level is requested, the results will be rounded to one significant figure.

1.8 For elements having a high channel and a low channel, the high channel is used when the sample exceeds the standard of the low channel.

2.0 SAFETY AND WASTE HANDLING

2.1 Toxicity or carcinogenicity of reagents used in this SOP has not been fully established. Each chemical should be considered as a potential health hazard and individual exposure should be minimized. Standard safety practices are to be followed such as the wearing of personal protective wear (safety glasses, gloves, lab coats) and referring to available MSD sheets. Follow the rules detailed in the Region 5 Central Regional Laboratory Health, Safety, and Environmental Compliance Manual and the Toxic Substance safety plans.

2.2 Radiation sources - intense ultra violet (UV) and radio frequency (RF) - are present when operating the ICP-OES spectrometer. Reasonable precautions to avoid exposure to these emitted radiation sources should be taken. This would include not looking directly at the ignited plasma or its reflection. The 3300DV is equipped with interlocks on the torch compartment door that will not allow the plasma to be ignited if the door is ajar. Unless routine maintenance is required in the torch compartment, the door should always be closed.

2.3 Within the spectrometer, lethal high voltages are present. Routine maintenance that would require the analyst to access high voltage areas should not be performed on the instrument unless the instrument is powered down and locked and tagged out. The instrument has a service contract on it and only trained, professional service engineers should perform complex repairs (i.e., non-routine) maintenance.

2.4 Unused portions of stock solutions, acids, calibration and analytical standard solutions, nebulizer waste and digested samples must be poured into the RED labeled waste containers.

3.0 SUMMARY OF METHOD

3.1 This method describes the determination of 29 elements dissolved and stabilized in aqueous acidic media which are then analyzed by the use of two specific ICP-OES units, namely the Perkin Elmer Optima 3300DV and 4300DV. As a matter of routine, representative sample sub-aliquots (50 mL for waters) are taken and digested with mineral acids using CRL microwave digestion procedures or beaker/hot plate digestion procedures using mineral acids and hydrogen peroxide. These digestion procedures are designed to insure that as much of the analytes that are available for recovery (i.e., total recoverable) are rendered soluble and relatively stable in aqueous acidic medium.

For description of the digestion methods see SOP METALS025 hot block digestion or METALS033 CLP-type

beaker digestion. It is noted that the acid strength of the standards in this method are matched only by digestion method METALS025 hot block digestion.

3.2 The resulting solutions are peristaltically pumped and pneumatically aspirated into aerosol mists which are conveyed in an argon gas stream through an inductively RF coupled region whereby a plasma is formed. Within the plasma, final desolvation, ionization, excitation and characteristic radiative emission for the analytes take place. The resultant emitted radiation is directed through the optics of the spectrometer where it is dispersed via a grating into component wavelengths that are indicative of specific elements present in the plasma. The intensity of the characteristic radiation is measured using a Charge- Coupled solid-state Detector (CCD).

3.3 The plasma can be viewed radially (from the side) and axially (down the central channel). If sample concentrations are expected to be low, axial, with a longer path length, will yield greater sensitivity. If concentrations are expected to be high, radial views will extend the linear range to greater concentrations. Since most elements have multiple analytical lines in this method, some were chosen to have one or more lines with axial view for sensitivity, but with a line viewed radially to extend the concentration range. The major elements are all viewed radially, because low concentrations of these elements were not needed for environmental decision-making.

3.4 The Perkin Elmer Optima ICP optics are purged with nitrogen which should always be used when conducting an analysis with this analysis method. MgF_2 optics along with the nitrogen gas purge facilitate the measuring of analyte lines in the far UV portion of the electromagnetic region of the spectrum. Emission intensities are counted at analyte peak locations and compared to counts obtained from calibration standards containing known amounts of specific analytes. The sample concentration values are calculated via the Perkin Elmer ICP WinLab software, typically using first order regression analysis calculations. For a given spectral line, one to three pixels of the detector are used to define the area under the peak. This integrated intensity is corrected for interferences by means of two interference correction models, an Inter-Elemental Correction (IEC) model and a Multi-component Spectral Fitting (MSF) model.

3.5 The concentration results and the integrated data are printed out. Integrations are variable length based upon intensity at the subarray. The average of several integrations is used for the reported value.

4.0 CAUTIONS

4.1 Potassium, due to ionization enhancement effects, is biased high by 10 to 20% in a typical sample with 50-100 mg Na/L. Potassium is typically less than 10 mg/L. For this reason, potassium is semi-quantitative under these conditions, and should be flagged accordingly.

4.2 To increase instrument stability, hoods in the room where instrument is located, in addition to hoods in the adjoining laboratory, should be closed.

4.3 For best performance, monitor the intensities of the internal standard for both axial and radial measurements. The intensities are affected by the condition of the purge windows, as well as the sample delivery system.

5.0 SAMPLE HANDLING AND PRESERVATION

5.1 All samples must have been collected using an approved and appropriate sampling plan.

5.2 Samples should be collected in polyethylene bottles with solid polypropylene caps. It is recommended that the bottles be pre-treated. The bottles may be soaked for twenty four hours with dilute nitric acid before use. The usual contaminants have been found to be lead and zinc. At least 200 mL of sample is requested to allow a duplicate and spike to be analyzed. More would be necessary if reanalyses were needed.

5.3 Water samples are preserved in the field to a pH < 2. Use 5 mL of 1:1 HNO_3 per liter of sample or blank. More acid may be used if necessary.

If the sample is not acidified for any reason, especially due to an anticipated hazard, an indication of this condition should accompany the samples and be directed to the attention of the Metals Group Leader. If pH is > 2, either the pH must be adjusted with HNO_3 and time allowed to re-solubilize the analyte(s) that may have adsorbed onto the container walls (16-hour minimum), or if the sample is extremely basic or highly buffered, and addition of acid would cause precipitation of the analytes of interest, this fact and the pH of the sample must be documented.

5.4 Samples can be held for six months prior to analysis.

6.0 INTERFERENCES

6.1 Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra. A certain amount of background is intrinsic to the plasma source itself. One component of this background is black-body radiation, which is the light emitted by any heated body. Another component is Bremsstrahlung, which results from collisions of the accelerated electrons and charged particles. The third component of the light emitted from the plasma itself is cyclotron radiation. This is the result of electrons being accelerated in a magnetic field, and is much stronger near the work coil. The sum of these effects is a broad emission band with the maximum at about 460 nm.

6.2 An important contribution to the background of the plasma is the result of reactions between components of the sample matrix or surrounding atmosphere. Nitrogen and oxygen combine in the envelope around the plasma to give excited NO molecules which emit a structured spectrum from about 180 to 230 nm. Water from the sample gives rise to OH emission, mostly in the 280 to 310 nm region. NH occurs about 360 nm; CO gives background from 180-200 nm; CN has spectra from 388 to 420 nm.

6.3 Another source of continuum background is the reaction of excited atoms from the sample with atmospheric oxygen. An example of this is the AlO emission from the oxygen cutoff (approx 180 nm to 230 nm).

6.4 Background emission and stray light can usually be compensated for by subtracting the background emission determined by measurements adjacent to the analyte wavelength peak. The locations selected for the measurement of background intensity will be determined by the complexity of the spectrum adjacent to the wavelength peak.

6.5. Line spectra are a very rich source of interference in plasma emission spectroscopy. Every component of the sample emits to some degree, and even the argon itself has a number of emission lines. Of the latter, only one channel (Na588.995) has a serious argon line interference.

6.5.1 Line spectral interferences can be grossly classified into two categories: overlapping lines, either through direct coincidence or within the resolving power of the instrument, and broadened lines. Directly overlapping lines of comparable strength are relatively rare, the appearance of the strong lines for Cd at 228.80 nm and As at 228.81 nm being an exception. More often, the analyte line is very near to a line from a major constituent, such as the Be 234.86 nm line which is within about twice the full width at half maximum (FWHM) of the Fe line at 234.81 nm.

6.5.2 Emission lines of elements have an intrinsic natural line width which is quite narrow, resulting in the large number of significant figures found in wavelength tables. The plasma is a very complex system;

these lines are broadened by a number of means. Doppler broadening results from the distribution of velocities of the emitting particles in the hot environment of the plasma. Collisional broadening takes many forms, from Van der Waals broadening by collision with neutral argon atoms, Stark broadening by collision of electrons with ions, and resonance broadening. The latter form of line broadening is most important when the interfering element is at high concentration. If an element has two lines which are close enough to be in resonance, and is present at high concentrations, collisions of the form

$$X^*_1 + X_g \text{ ---> } X_g + X^*_2$$

can take place, where X_g refers to ground state X and X^*_1 and X^*_2 are the two resonance excited states. The Al lines gain a significant background from the Ca lines which are well separated at low levels.

6.6 Spectral overlaps may be avoided by using an alternate wavelength or can be compensated for by the use of Inter-Element Correction (IEC) equations or Multi-component Spectral Fitting (MSF).

6.6.1 Interelement correction is a spectral interference correction technique in which emission contributions from interfering elements that emit at the analyte wavelength are subtracted from the apparent analyte emission after measuring the interfering element concentrations at other wavelengths.

6.6.2 Multi-component spectral fitting (MSF) is an algorithm whereby a model is built of spectra collected from blanks, analyte, and potential interferents. This is an option that is no longer used at CRL.

6.7 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they may be ameliorated by use of an internal standard. Yttrium is the most common choice of internal standard. If it is used, the same amount must be added to all standards and samples. Both ICPs are equipped with a second peristaltic pump to be used for addition of the internal standard.

6.8 If high suspended solids are apparent in the samples, the samples should be filtered or centrifuged prior to analysis.

6.9 High dissolved solids can contribute to salting out on the tip of the nebulizer and this will affect plasma performance. If high dissolved solids are suspected in the samples, monitor the nebulizer and take corrective action if necessary.

6.10 Chemical interferences include molecular-compound formation, ionization effects, and solute-vaporization effects. Normally, these effects are not significant with the ICP-OES technique. The most common interference of this type can be seen in the analysis of an alkali metal (e.g., K) in the presence of a high concentration of another alkali metal (e.g., Na). Alkali metals are easily ionized, but are determined by emission from the neutral species.

A high concentration of one will supply an excess of electrons to the plasma, boosting the neutral atom population of the less concentrated alkali metal, causing an enhancement relative to the standards.

Please note: This phenomena was studied during method development on the Perkin Elmer 3300DV. The studies showed that those elements that are being determined axially are not affected. However, the transition elements, that are determined radially, will be affected in a highly alkali matrix.

6.11 Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer, and from the buildup of sample material in the plasma torch and spray chamber. The site where these effects occur is

dependent on the element and can be minimized by flushing the system thoroughly between samples.

7.0 APPARATUS

7.1 Perkin-Elmer Optima 3300 DV Inductively coupled argon plasma atomic emission spectrometer with 32-bit software, equipped with:

7.1.1 Neslab CFT-33 refrigerated recirculator,

7.1.2 Perkin Elmer AS91 autosampler,

7.1.3 Perkin Elmer peristaltic sample pump,

7.1.4 Gilson peristaltic Internal Standard pump,

7.1.5 GemCone (Conespray) nebulizer,

7.1.6 Cyclonic spray chamber, and

7.1.7 Dell Optiplex GX270 computer, Dell monitor, Hewlett Packard DeskJet 694C (or equivalent).

7.2 Perkin-Elmer Optima 4300 DV Inductively coupled argon plasma atomic emission spectrometer with 32-bit software, equipped with:

7.2.1 Polyscience refrigerated recirculator,

7.2.2 Perkin Elmer AS93 autosampler,

7.2.3 Perkin Elmer peristaltic sample pump,

7.2.4 Gilson peristaltic Internal Standard pump,

7.2.5 GemCone (Conespray) nebulizer,

7.2.6 Cyclonic spray chamber, and

7.2.7 Dell Optiplex GX270 computer, Dell monitor, Hewlett Packard LaserJet 4050 (or equivalent).

7.3 Argon Supply (GP55 Liquid)

7.4 Nitrogen Supply (GP55 Liquid)

7.5 Volumetric flasks, Class A glass, and Class B polyethylene

7.6 30-mL polystyrene cups

7.7 50-mL centrifuge tubes

7.8 Eppendorf pipets and tips

8.0 REAGENTS AND STANDARDS

8.1 Nitric Acid - Ultrex , Baker Instra-Analyzed or GFS Chemicals redistilled or equivalent.

8.2 Hydrochloric Acid Ultrex, Baker Instra-Analyzed or equivalent.

8.3 Water - Laboratory distilled water is passed through a mixed bed resin column before use. The water is called "Super Q," after the column used. All water used for ICP analysis and standards is Super Q.

8.4 Triton-X 100 wash solution (2% HNO_3, 0.1% Triton-X 100) - In a 1-liter volumetric flask, 20 mL HNO_3 and 1 mL Triton-X 100 is added to Super Q water.

Please note: Sonication will speed dissolution of the Triton-X 100.

8.5 Plasma-grade certified 1000 mg/L standards. These standards must be of sufficient purity that mixing standards will not result in addition of unknown amounts of other elements, possibly affecting the final concentration of the analyte. For this reason High-Purity Standards and Spex Standards or equivalent are recommended for mixed standards.

Please note: **All calibration and analytical standard preparations must be documented in the CRL PE 3300DV/4300DV ICP Standard Prep. Record. All solution bottles shall be properly labeled with the contents, the preparers initials, the date of preparation, and the acid matrix. Separate standards/solutions and separate preparation records must be maintained by the ESAT staff.**

8.6 The following table outlines the standards used for calibrating the instrument. The standards are prepared from Inorganic Ventures Environmental Solutions (or equivalent):

Standard ID	Stock ID	Element(s)	Stock Conc. (mg/L)	Final Conc. (mg/L)	Acid Matrix
CAL BLANK			0	0	1% HNO_3 0.5% HCl
CAL 1	Inorganic Ventures WW-CAL-1	As Ca Sb Se Cd Cu* Mn B Ba Sr Ag*	1000 500 200 100 500	10 5 2 1 5*	1% HNO_3 0.5% HCl
CAL 2	Inorganic Ventures WW-CAL-2	K* Mo Na Ti Li	2000 1000 500	20* 10 5	1% HNO_3 0.5% HCl
CAL 3	Inorganic Ventures WW-CAL-3	P* Ce Co V	1000 200	10 2	1% HNO_3 0.5% HCl
CAL 4					
CAL 4A	Inorganic Ventures WW-CAL-4A	Al Cr Zn Hg*	1000 500 200	10 5 2*	1% HNO_3 0.5% HCl

Standard ID	Stock ID	Element(s)	Stock Conc. (mg/L)	Final Conc. (mg/L)	Acid Matrix
CAL 4B	Inorganic Ventures WW-CAL-4B	SiO_2* Sn	1000 400	10* 4	1% HNO_3 0.5% HCl
CAL Ag/K	High Purity	Ag Cu K	1‡ 1000 10,000	0.1 2 200†	1% HNO_3 0.5% HCl
CAL 5	Inorganic Ventures WW-CAL-5	Fe Pb Mg Tl Ni Be	1000 500 200 100	10 5 2 1	1% HNO_3 0.5% HCl
HI CAL	High Purity	Al Ca Fe Mg Na	10,000	500 200†	1% HNO_3 0.5% HCl

* Present in the standard, but not currently used for calibration

‡ Silver in the Ag/K standard is made from a 1.00 mg Ag/L intermediate which is made from diluting 0.1 mL of 1000 mg Ag/L stock into a 100 mL volumetric containing 10 mL of 1:1 HCl. This intermediate is stable in the 5% HCl matrix.

† Note that potassium and sodium may extend to 500 mg/L for the 4300DV.

Please note: Calibration standards are prepared in 100 mL volumetric flasks. Add 50 mL Super Q, 1 mL 1:1 HCl, and 2 mL 1:1 HNO_3 to each flask. Add the required volume of stock standard(s) and bring to volume. Transfer the working standard to the designated 125 mL Nalgene calibration standard bottle. The Cal Blank is made in a polyethylene volumetric flask. This is to avoid introducing contaminants in the calibration blank, possibly biasing subsequent results low.

Please note: **When preparing standards, always transfer the stock standards to a fresh 30 mL polystyrene cup to avoid contamination. Always close the bottle immediately after pouring to maintain the stack standard concentration. Do not leave standards or acids in these vessels for extended periods of time, as they will pick up contaminants such as zinc.**

8.7 The traceability of both the single-element standards and the Inorganic Ventures Environmental Solutions (or equivalent)is given on the Certificate of Analysis sheet that is provided by the manufacturer. This certificate is kept in a ring binder in the ICP laboratory.

8.8 The following table outlines the analytical standards used during the course of an analytical run. The standards are prepared from a second source, separate from the source used to prepare the calibration standards, Inorganic Ventures Environmental Solutions (or equivalent):

Standard ID	Stock ID	Element(s)	Stock Conc. (mg/L)	Final Conc. (mg/L)	Acid Matrix
LCB			0	0	1% HNO_3 0.5% HCl
LCM1	Inorganic Ventures (second source)	K P* SiO_2* Sn Tl As Hg Pb Sb Al B Ba Be Ca Cd Ce Co Cr Cu Fe Li Mg Mn	500 200 100	5 2 1	1% HNO_3 0.5% HCl

Standard ID	Stock ID	Element(s)	Stock Conc. (mg/L)	Final Conc. (mg/L)	Acid Matrix
	QCP-QCS-1 QCP-QCS-2	Mo Na Ni Sr Ti V Zn Ag*	 25*	 0.25	
LCM2	Spex	Ag‡	1	0.05	1% HNO_3 0.5% HCl
HI LCM	Inorganic Ventures EPA-V-3C	Al Ca Fe K Na Mg	1000 600	100 60	1% HNO_3 0.5% HCl

* Not used in this standard for QC purposes.

‡ Silver in the LCM2 standard is made from a 1.00 mg Ag/L intermediate which is made from diluting 0.1 mL of 1000 mg Ag/L stock (Spex for second source) into a 100 mL volumetric containing 10 mL of 1:1 HCl. This intermediate is stable in the 5% HCl matrix.

Please note: Analytical standards are prepared in 100 mL volumetric flasks. Add 50 mL Super Q, 1 mL 1:1 HCl, and 2 mL 1:1 HNO_3 to each flask. Add the required volume of stock standard(s) and bring to volume. Transfer the working standard to the designated 125 mL Nalgene analytical standard bottle. The LCB is made in a polyethylene volumetric flask.

Please note: When preparing standards, always transfer the stock standards to a fresh 30 mL polystyrene cup to avoid contamination. See the note in section 8.6.

8.9 The following table outlines the Reporting Limit Check (RLC) stock standard for the 3300DV. The standard is prepared from High Purity Environmental Solutions (or equivalent):

Element	RLC Stock Conc. (μg/L)	High Purity (HP) Stock Conc. (mg/L)	Vol. HP Stock Used (mL)	Final Vol. (mL)	Working RLC Conc. (μg/L)
Ag	500	1,000	0.5	1,000	5.0
Al	5000	1,000	5.0	⇓	50
As	1500	1,000	1.5	⇓	15
B	10,000	1,000	10.0	⇓	100
Ba	200	1,000	0.2	⇓	2.0
Be	100	1,000	0.1	⇓	1.0
Ca	5000	1,000	5.0	⇓	50
Cd	100	1,000	0.1	⇓	1.0
Ce	5000	1,000	5.0	⇓	50
Co	200	1,000	0.2	⇓	2.0
Cr	300	1,000	0.3	⇓	3.0
Cu	400	1,000	0.4	⇓	4.0
Fe	2000	1,000	2.0	⇓	20
K	80,000	10,000	8.0	⇓	800
Li	2500	1,000	2.5	⇓	25
Mg	2000	1,000	2.0	⇓	20
Mn	200	1,000	0.2	⇓	2.0
Mo	1000	1,000	1.0	⇓	10
Na	20,000	10,000	2.0	⇓	200
Ni	200	1,000	0.2	⇓	2.0

Element	RLC Stock Conc. (μg/L)	High Purity (HP) Stock Conc. (mg/L)	Vol. HP Stock Used (mL)	Final Vol. (mL)	Working RLC Conc. (μg/L)
Pb	2000	1,000	2.0	⇓	20
Sb	3000	1,000	3.0	⇓	30
Se	3000	1,000	3.0	⇓	30
Sn	1000	1,000	1.0	⇓	10
Sr	200	1,000	0.2	⇓	2.0
Ti	400	1,000	0.4	⇓	4.0
Tl	3000	1,000	3.0	⇓	30
V	200	1,000	0.2	⇓	2.0
Zn	3000	1,000	3.0	⇓	30

Please note: The RLC stock standard is prepared in a 1000 mL volumetric flask. Add 50 mL Super Q, 20 mL Conc. HCl, and 20 mL Conc. HNO_3 to the flask. Add the required amount of High Purity Stock standard (see table above) to the flask and bring to volume. Transfer the stock RLC standard to a 1000 mL Nalgene bottle.

Please note: The RLC working standard is prepared in a 100 mL volumetric flask. Add 50 mL Super Q, 1 mL 1:1 HCl, and 2 mL 1:1 HNO_3 to the flask. Add 1 mL of the stock RLC standard and bring to volume. Transfer the working standard to a 125 mL Nalgene bottle.

Please note: When preparing standards, always transfer the stock standard to a fresh 30 mL polystyrene cup to avoid contamination. See note in 8.6.

8.10 The following table outlines the Reporting Limit Check (RLC) stock standard for the 4300DV. The standard is prepared from High Purity Environmental Solutions (or equivalent):

Element	RLC Stock Conc. (μg/L)	High Purity(HP) Stock Conc. (mg/L)	Vol. HP Stock Used (mL)	Final Vol. (mL)	Working RLC Conc. (μg/L)
Ag	500	1,000	0.5	1,000	5.0
Al	10,000	1,000	10	⇓	100
As	1,500	1,000	1.5	⇓	15
B	10,000	1,000	10	⇓	100
Ba	200	1,000	0.2	⇓	2.0
Be	100	1,000	0.1	⇓	1.0
Ca	6,000	1,000	6.0	⇓	60
Cd	100	1,000	0.1	⇓	1.0
Ce	10,000	1,000	10	⇓	100
Co	200	1,000	0.2	⇓	2.0
Cr	400	1,000	0.4	⇓	4.0
Cu	500	1,000	0.5	⇓	5.0
Fe	2,000	1,000	2.0	⇓	20
K	20,000	10,000	20	⇓	2,000
Li	2,500	1,000	2.5	⇓	25
Mg	2,000	1,000	2.0	⇓	20
Mn	100	1,000	0.1	⇓	1.0
Mo	400	1,000	0.4	⇓	4.0
Na	40,000	10,000	4.0	⇓	400
Ni	200	1,000	0.2	⇓	2.0
Pb	1,500	1,000	1.5	⇓	15
Sb	2,000	1,000	2.0	⇓	20
Se	3,000	1,000	3.0	⇓	30

Element	RLC Stock Conc. (μg/L)	High Purity(HP) Stock Conc. (mg/L)	Vol. HP Stock Used (mL)	Final Vol. (mL)	Working RLC Conc. (μg/L)
Sn	1,000	1,000	1.0	⇓	10
Sr	100	1,000	0.1	⇓	1.0
Ti	500	1,000	0.5	⇓	5.0
Tl	2,000	1,000	2.0	⇓	20
V	600	1,000	0.6	⇓	6.0
Zn	4,000	1,000	4.0	⇓	40

8.11 The following table outlines the Spectral Interference Check (SIC) standards. These standards must be analyzed at least once each analysis day directly following instrument calibration. The components of these standards were chosen based on spectral evidence found during method development which points to possible areas of weakness in the interference correction models. The analyst must fill-out the SIC standard log (located at the instrument) every time the standards are analyzed. The standards are prepared from High Purity Environmental Solutions (or equivalent):

SIC SOLUTION	ELEMENT(S)	CONCENTRATION	ACID MATRIX
1	Co	10 PPM	1% HNO_3 0.5% HCl
2	Ce	10 PPM	1% HNO_3 0.5% HCl
3	Cr	10 PPM	1% HNO_3 0.5% HCl
4	Fe	300 PPM	1% HNO_3 0.5% HCl
5	Mn	10 PPM	1% HNO_3 0.5% HCl
6	Mo	10 PPM	1% HNO_3 0.5% HCl
7	Cu	10 PPM	1% HNO_3 0.5% HCl
8	Ti	10 PPM	1% HNO_3 0.5% HCl
8	V	10 PPM	1% HNO_3 0.5% HCl

Please note: The SIC standards are prepared in 100 mL volumetric flasks. Add 50 mL Super Q, 1 mL 1:1 HCl, and 2 mL 1:1 HNO_3 to the flask. For solution 1, add 1 mL each of the Co and V High Purity stock standard (1,000 mg/L) and bring to volume. For solutions 2-3 and 6-8, add 1 mL of the appropriate High Purity stock standard (1,000 mg/L) and bring to volume. For solution 4, add 3 mL of the stock Fe High Purity standard (10,000 mg/L) and bring to volume. For solution 5, add 2 mL of the stock Mn High Purity standard (1,000 mg/L) and bring to volume. Transfer each of the solutions to clean 125 mL Nalgene bottles.

8.12 The following table outlines Spike Solution A and B. These solutions are added to the sample designated for matrix QC audits at the time of digestion. The solutions are prepared from High Purity Environmental Solutions

(or equivalent):

Spike Solution	Elements	Stock Conc. (mg/L)	Amount Added (mL)	Final Conc. (mg/L)*
A	Be	0.5	1	0.01
	Ag	1.25		0.025
	Cd	2.5		0.05
	Co Cr Cu Li Mo Ti V	5		0.1
	As Ba Mn Ni	10		0.2
	Ce Pb Sb Se Sn Tl	25		0.5
B	Al B Fe Sr Zn	50	1	1
	Mg	1000		20
	K	1250		25
	Ca Na	2500		50

* of analyte in digestate.

Please note: Spiking solutions A and B are prepared in 1,000 mL and 200 mL volumetric flasks, respectively. Add 20 mL Super Q to each volumetric flask. Add 50 mL Conc. HCl to the 1000 mL volumetric, and 10 mL Conc. HCl to the 200 mL volumetric. Add the required volume of stock standard(s) and bring to volume. The High Purity stock standard concentrations are all 1,000 mg/L for spiking solution A. The High Purity stock standard solutions are all 10,000 mg/L for spiking solution B. Transfer each spiking solution to the designated 1,000 mL spiking solution bottle.

Please note: When preparing the spiking solutions, always transfer the stock standards to a fresh 30 mL polystyrene cup to avoid contamination. See note in 8.6.

9.0 PROCEDURE

9.1 Turn the RF toggle switch on the left side of the instrument to the "on" position. Turn on the shear gas air supply (the valve is located on the wall behind the instrument). Turn the autosampler power supply (located under the instrument) toggle switch to "on" position. Power up the computer and the printer by flicking the toggle switch on the power strip to the "on" position. Engage the pump tubing on both the sample peristaltic pump and the internal standard peristaltic pump, making sure that the pump tubing tension arm is fully engaged on all tubes. If the pump tubing is new, stretch the tubing several times by grasping the tubing on the ends and pulling gently.

Please note: It is recommended that the hood sash be kept in a lowered position while the plasma is on, as the canopy is operating on the same fan. If manipulations must be performed in the hood while the plasma is on, the sash should be returned to the lowered position as soon as possible after completion of the task.

9.2 Fill the wash water reservoir with Triton-X 100 wash solution (2% HNO_3, 0.1% Triton-X 100). Place the internal standard line in the Yttrium reservoir.

9.3 Check argon supply and turn the pressure on the nitrogen purge gas supply to 35 psi. Check chiller (Temperature should be set at 17°C).

9.4 Enter ICP Winlab software. Open the current water method file. This method will be labeled as **water_mmddyy**, where mmddyy is a date with month, day, year.

Please note: The Method Editor window can be opened to see (and edit) method parameters. However, changes to the method may **not** be saved without approval of the Metals Group Leader. If the method is changed, with

approval from the Metals Group Leader, save the modified method to a different name, and document changes in the instrument log book.

9.5 Open the Plasma Control window, click the toggle switch in the window to begin plasma ignition sequence. Once the plasma has been successfully ignited, observe plasma through viewing window to ensure plasma is stable. Allow at least an hour for the plasma to stabilize before beginning the run. Have the probe in the wash solution and the internal standard pump running at least one-half hour before analysis begins.

9.6 If the analyst has a Work Space saved, open it now by going to File on the tool bar, then Open and then Work Space (It is recommended that the analyst save his or her own Work Space on the system).

Please note: The save Work Space option of the software allows the analyst to save a series of windows that are open on the screen and are routinely used during the course of an analysis (i.e., Results window, Automated Analysis Control window, Spectra window, etc...). It also saves information like Results file, Sample Information file and Method. The analyst **must use caution** when opening his or her Work Space to insure that the correct method is being used and that the results are being saved to the appropriate results file.

9.7 Open the Sample Information Editor to create a Sample Information file. Enter the information that is common to all samples (e.g., the Batch Number, Analyst, sample batch description, etc.). Then, enter the information that is specific to each sample (e.g., A/S Location, Sample ID, Dilution and Analyze QC Before fields). By clicking **New** after entering the Sample Information Editor, the analyst may select a template for the .sif file. In the Administrator folder, there is a water template with all the desired fields.

Please note: Analytical QC are cued within the method to run automatically at certain times during the course of the analytical run (i.e., after the initial calibration and at the end of the run). Use the Method Editor window to see when the analytical QC are cued to run automatically. If all or some of the QC standards must be run additional times during the analytical run, the QC standards must be identified in the "Analyze QC Before" field.

9.8 After creating the Sample Information File, save it using the current date as the file name (use the following convention: MMDDYY.sif, where MM is the two digit month, DD is the two digit day, and YY is the two digit year). Go to the Set-Up page in the Automated Analysis Control window and specify the Results file name by clicking on the Browse button. Enter a file name using the same naming convention as used for the Sample Information file (a brief description of the results file can also be entered here). Enter the Sample Information file name created earlier. Load the autosampler. Fresh calibration blank and LCB are made each day, as trace amounts of contaminants, such as zinc accumulate in the centrifuge tubes over time.

9.9 On the Set-Up page of the Automated Analysis Control window, click the box next to Hg Realign. This will trigger a Hg realignment to be performed at the beginning of the analysis (the Hg Realign must be performed at least once per analysis run).

Please note: If the analyst has saved his or her Work Space and the Hg Realign box has been checked in the Automated Analysis Control window before saving the Work Space, the Hg Realign box will remain checked every time the Work Space is opened and a Hg realignment will be performed automatically at the beginning of the automated analysis.

9.10 On the Analyze page of the Automated Analysis Control window review the sequence of the standards and samples to be run in the "sequence pane."

Please note: The analytical sequence will not mirror what was entered in the Sample Information Editor. The calibration standards and automated QC's will appear in the sequence pane, but will not be entered by the analyst in the Sample Information Editor. Calibration standards and automated QC's are entered in the Method Editor

series of windows.

9.11 A typical analytical sequence is as follows:

9.11.1 Instrument calibration standards

9.11.2 Quality control standards (i.e., LCB, LCM1, LCM2, LCMHI and Reporting Limit Check standard).

Please note: High concentration check standards (e.g., LCMHI) should be followed by at least one blank wash sample to minimize carryover.

9.11.3 RLC and SIC solutions, generally followed by the periodic check standards.

9.11.4 Series of sample digests (10 or fewer) including digested QC, spike blanks, LCS (if necessary) and matrix duplicates & spikes.

9.11.5 Periodic quality control check standards (again, the LCB, LCM1, LCM2 and LCMHI).

9.11.6 Another group of ten samples or less, if present, and periodic quality control check standards until finished.

9.11.7 Final quality control check standards (i.e., LCB, LCM1, LCM2 and LCMHI) are analyzed at the end after all the samples and digestion QC.

Please note: If changes are made to either the automated QC's in the Method Editor window or the samples/standards in the Sample Information Editor, the Rebuild List button on the Analyze page in the Automated Analysis Control window must be clicked to update the sequence pane.

9.12 After reviewing the analytical sequence click on the **Analyze All** button on the Analyze page of the Automated Analysis Control window. This will initiate an analysis run in which all calibration standards, samples and QC standards will be run. It is possible to analyze the calibration standards separately by choosing the **Calib** button, but normally one will use **Analyze All**. No samples may be analyzed before calibration standards have been run that day.

Please note: The method currently does not have pass/fail criteria triggered to have the instrument automatically perform certain tasks should a QC standard fail to meet the pass criteria. The analyst must therefore monitor the status of the analysis to ensure that all the QC audits are successful (i.e., within the control limits for the specific QC audit).

9.13 When running high and low level samples together, be alert for memory effects. The Triton-X 100 solution reduces memory effects considerably. However, carryover may still be a problem with some samples. If carryover is detected, stop the automated analysis by clicking on the Analyze All button once again and follow the appropriate instructions on the pop-up window that appears.

Allow the system to flush completely with the Triton-X 100 wash solution. Once complete, continue the analysis at the point where it was interrupted. If high samples are suspected, a wash may be inserted into the .sif file.

9.14 When the analysis is finished, replace the Triton-X 100 wash and the yttrium internal standard solution with laboratory distilled water. Flush water through the system for 5 to 10 minutes while the plasma is still on. When this is complete, turn off plasma by clicking on the "on/off" toggle switch on the Plasma Control Window. Be certain the Plasma Flow has been set to zero before leaving the software.

Disengage sample and internal standard pump tubing and release the tension on the tubing. Turn off the RF generator by clicking the toggle switch to the "off" position. Turn off the autosampler controller by clicking the toggle switch to the "off" position. Shut down the ICP WinLab software and turn off the house air. Finally, turn the pressure on the nitrogen supply down to just unpegged on the regulator.

9.15 Data should be uploaded to the R5CRL server as soon as possible after completion of the run. Raw data to be uploaded include the database file, which requires a library, and the .sif file. Export files, wherein data are extracted and placed in a comma delimited file, may be uploaded at this time.

9.15.1 If not already logged into the R5CRL server, close all programs and connect as a different user, logging into both the R5CRL server and the XP workstation.

9.15.2 Using Windows Explorer, go to "Volx on 'R5crl' (H:)," where x refers to the volume number (Vol1 for CRL). Double click on the Metals folder that appears. Highlight the folder with the appropriate analyst's name beside it.

9.15.3 Click on File on the command line at the top of the window. Highlight the word New and highlight and click on the word Folder. This will allow the analyst to create a new folder under his or her directory. Create a folder named for the batch number of the samples in the run. Create subfolders for raw data and reports as described in GEN001 (Reference 13.12).

9.15.4 Open Data Manager. Under Tasks, find the function "Create New Library." Choose the subfolder just created for raw data as the destination for the library. The error "No Current Record" will appear, but this only means the library just created contains no data.

9.15.5 With the data file to be copied highlighted, choose Copy from the taskbar, and the new library created above as the destination.

9.15.6 The Export function on the taskbar may be used to copy the data to be used for the reports into the reports subdirectory created above. The data is now in a comma delimited file for further manipulation with a spreadsheet or other data reduction software. This is easiest if the same Design is used repeatedly for the same type of sample.

9.15.7 One Design is used for upload of data to Data Tool. This should be modified only by choosing the analytes and lines to be uploaded and the destination folder. All fields are chosen, and it creates a comma delimited .prn file and is used with Data Tool as described in section 12.2.4 and 12.2.5.

9.15.8 Use Explorer to copy the .sif file(s) into the raw data subfolder.

10.0 QUALITY CONTROL

10.1 Instrument Check Audits

10.1.1 In general, 10% frequency of running instrument control check audits is used, meaning sets of the audits named below shall bracket every 10 field samples or fraction thereof. The exception is the RLC that is run only at the beginning or at the beginning and end of a run. This will mean that more digests than 10 may be run between the sets of instrument audits, because at least one set of digestion QC audits will accompany those 10 field samples. All limits given herein will be updated with limits derived from historical data when at least 10 points are available. Thereafter, the limits will be updated periodically with at most the most recent 20 points. These limits will be included as an addendum to the SOP. IDOC's can be used to derive interim limits.

Analytical QC Audit ID	Control Limits*
LCB (TABLE 7.7):	± Method Detection Limits (µg analyte/L)
LCM1, LCM2 & LCMHI (TABLE 7.7):	100 ± 10% Recovery
RLC (TABLE 7.8)	100 ± 20% Recovery

* Any values beyond these limits are flagged.

10.1.2 The solutions analyzed as SIC standards (Section 8.11) are those with which the MSF model has been shown to be imperfect relative to the reporting limit of the analytes that are interfered with. In an ideal model, the contribution from the interfering element would be completely removed, and noise in the signal would be the only component remaining affecting the analyte reading. Some contribution from an interferent may result in a false positive or negative. The analysis of the SIC demonstrates the magnitude of this error, and the analyst will evaluate the relevance of this error and if this error has significant effect on the particular samples being analyzed. **The significance of the error, if any, must be explained in the narrative.** No attempt will be made to further correct the results. If after ten or more analyses of the SIC solution, the error is statistically the same within an acceptable range (about ± 10%, or within a small multiple of the RL), then the frequency of these checks can be reduced. If the result varies widely, then the model should be reexamined, and samples reanalyzed after reconstructing the model. Periodically, at least once per quarter initially, SICs will be examined for all potential interferents at the 10 mg/L level, or up to levels appropriate to the typical concentration for more common interferents.

10.2 Digestion Audits:

A complete set of digestion QC are required for every 10 field samples or less with the exception of the digestion blank (LRB) and the digested spike blank (LFB). Only one LRB and LFB is required to accompany each sample batch regardless of the number of samples in the batch. Additional blanks and spike blanks may be digested with the sample batch at the analyst's discretion.

10.2.1 Digestion Blank (LRB) - The same volume of Super Q water as used for the samples (typically 50 mL) treated as a sample. All steps used for the samples (e.g., filtration or centrifugation) are also performed on the blank. The digestion blank demonstrates that there is no contamination in the reagents or glassware. The limit for this audit is ± the MDL (Any values beyond these limits are flagged).

10.2.2 Digestion Matrix Duplicate (LD1) - This is a second aliquot of a field sample treated as a separate sample. Duplicates give an indication of sample homogeneity and consistency of subsampling. The limit for this audit is a relative percent difference (RPD) of ±10% or, near the detection limit, an absolute difference of ± the MDL (Any values beyond these limits are flagged). RPD is defined as:

Where S is the sample result, and D is the duplicate result.

10.2.3 Digestion Matrix Spike (LSF) - This is a second aliquot of a field sample to which has been added the spiking solutions given in section 8.12. Current practice is to add 1 mL each of the two solutions, A and

B, to a 50 mL aliquot. This spiked sample is then processed the same as a regular sample. Low spike recovery on three or more elements may indicate poor digestion results. For a complex sample low spike recovery may indicate interferences; or, when the duplicate result is taken into account, may indicate a lack of homogeneity or a failure to obtain a representative subsample. A low spike may also be caused by instrument drift. The instrument QC will confirm any instrument drift or nebulizer problem. The limit for this audit is a percent recovery defined as:

$$\% \text{ Rec} = ((Sp-S)/A) \times 100$$

where % Rec is the percent recovery, Sp is the result in common units (say mg/L) for the spiked sample, S is the result for the sample in those same units, and A is the added spike in those same units. The limit for this audit is 100 ± 15% (Any values beyond these limits are flagged), up to the point where the sample concentration is twice the added spike. At that point the audit is no longer considered valid. Spiked samples may exceed the linear range for a given channel. These should be diluted and rerun just as any sample would be diluted and rerun for that element.

10.2.4 Digested Spiked Blank (LFB) - This is a blank as in 10.2.1, to which has been added the spiking solutions added in 10.2.3. The equation is the same as for 10.2.3, except the sample is the digestion blank. The limit for this audit is 100 ± 15% (Any values beyond these limits are flagged).

10.2.5 The frequency of digestion QC should be one set of blank, duplicate and spike per field sample batch or one per 10 field samples, whichever is more frequent. The LFB need be performed only once per digestion set. If the field sampler has designated a sample for matrix QC, that is the sample to be used. Additional samples may be chosen at the analyst's discretion, save for designated field blanks. A field blank may not be used for the duplicate or spiked sample.

10.3 Acceptance of Run/Element Data:

10.3.1 When analyzing simultaneously for many elements, it is statistically predictable that some audits will be outside the stated limits due to random error. However, there is no generally accepted statistical method for determining that an analysis is in control when an audit has exceeded control limits. If an element of interest to the requestor is out of control for an audit, the samples shall be re-analyzed, or re-prepared and re-analyzed, as needed. These steps may be avoided if, after discussion with the requestor, the failed audit is found to have little effect on the intended use of the data. Data Quality Objectives (DQOs) should be part of a quality assurance project plan (QAPP) received with the samples. These should give action limits and intended use of the data.

If these are not present, discussion with the sampler or the project manager can help with the decision whether reanalyses is necessary. For example, if an element is found in the blank above the detection limit, or the spike recovery for the element is high, but all results for the element are below the action level for the Program, the data are useable.

10.3.2 The run must be reviewed for systematic errors. Systematic errors may be found in at least three categories: Contamination, which may be random or consistent; drift of baseline; or drift of slope. This by no means covers all types of error, rather only the most common. Evidence of systematic error would be cause for rejection of an element from a run or, in extreme cases, rejection of the run.

10.3.2.1 Systematic errors from low level contamination are difficult to spot, but can be diagnosed by examination of blanks and field blanks. Duplicates and spikes may also show low level contamination if the concentration in the sample itself is low. Field blanks should be confirmed to show that the contamination does not arise from the laboratory. One

member of a duplicate or spike pair may be elevated by contamination, throwing the audit out of control. The pattern of all the audits from a digestion run must be examined for evidence of contamination. The Group Leader or QC Coordinator may choose to have the run redigested for that element.

10.3.2.2 Systematic errors from baseline drift, if positive, may appear to be similar to the contamination mentioned above. It is easily confirmed while running by aspirating the calibration blank. It is less easily diagnosed after the run is over. Negative drift is equally to be avoided because false negatives can result.

It is quite possible that the other audits, LCM's, duplicates and spikes, may be in control even if the blanks show unacceptable drift.

10.3.2.3 Drift of slope rarely affects only one channel. The nebulizer may clog, or the plasma may get hotter or cooler in the course of the run. These problems will affect different elements differently, and may cause drift in different directions. The instrument QC should be examined not only to show if they are in or out of control, but for trends. For example, a low LCM, within control but biased low, may indicate why a spike for that element becomes flagged. Drift may affect only a portion of a run, in which case only that portion needs to be rerun.

10.4 The measurement of the method detection limit is performed by the procedure specified in CRL SOP GEN012 (Reference 13.13). The reporting limit is determined to be 3 to 5 times this value, and this becomes the concentration of the RLC solution mentioned in sections 8.9 and 8.10. How often the MDL must be determined is a function of instrument conditions and historical quality control data.

10.4.1 If the instrument has had major work done to the spectrometer, then a measurement of a new MDL must be preformed.

10.4.2 If there is a change to the SOP or the instrument method, such as changing forward power, changing wavelengths, correction scheme, mode of viewing, or a change in the calibration range.

10.4.3 If there is a trend observed in the historical data obtained on the digestion blank (LRB) or on the recovery of the RLC, as displayed in the control charts or range charts (Reference 13.14), then a measurement of a new MDL must be performed. If there is a question about what constitutes a significant trend, consult the Metals Group Leader.

10.5 The following QC samples are prepared and analyzed at the minimum frequency indicated, in addition to other QC discussed in this SOP, unless otherwise specified by GLNPO. MDLs can be located in Section 1.0. All samples should be recorded and entered into GLENDA using GLNPO's QC identification codes.

QC Sample Type		GLENDA QCID	Frequency	Acceptance Criteria
External	Field Reagent Blank	FRB	One per basin	To be determined
	Field Duplicate	FD1	One per basin	RPD ≤ 20%
	Laboratory Duplicate	LD1*	One per basin	Difference ≤ 2.0 μg/L
Internal	Blank Check, LCB	CLB	10% frequency of running instrument control checks or 1 per 10 samples, whichever is	± MDL μg/L

			more frequent	
	Low Check Standard, LCM1 Low Check Standard, LCM2 High Check Standard, LCMHI	CL1 CL2 CH1	At the beginning & end of each batch or 1 per 40 samples, whichever is more frequent (unless otherwise agreed upon with GLNPO)	100% ± 10% Recovery (unless otherwise defined by GLNPO)
	Reporting Limit Check, RLC	LPC	10% frequency of running instrument control checks or 1 per 10 samples, whichever is more frequent	100% ± 20% Recovery
	Digestion Blank, LRB	LRB	One per batch	± MDL μg/L
	Digestion Matrix Duplicate, LD1 (if necessary as defined by lab)	LD2	One per batch or 1 per 10 samples, whichever is more frequent	RPD ≤ 10% or, near the detection limit, an absolute difference of ± MDL μg/L
	Method Detection Limit, MDL	MDL	Per Section 10.4	To be determined

* GLNPO creates a laboratory duplicate in the field and ships this sample to the laboratory with the RFS.

11.0 PREVENTATIVE MAINTENANCE

11.1 Inspect the pump tubing before operating. Tubing can be stretched gently 10 times by hand before installation. A push pin is inserted into the tubing before installation to stretch it. When pump is not in use, release the pressure plate and release the tubing to prevent flat spots from forming.

11.2 The following should be regularly checked:

11.2.1 Air filters: clean or replace as necessary, typically twice per year.

11.2.2 Pneumatic filters: check the argon dryer filter, and argon and nitrogen filters for moisture.

11.2.3 Neslab Chiller: flush out chiller every six months or as needed, typically twice per year. Inspect the water filter installed on the chiller and replace the water filter element as needed. Inspect the brass mesh filter on the side of the pump inside the chiller at least annually. To fill the chiller, use only ***distilled*** or ***reverse osmosis*** water. The volume of the chiller is about 6 L.

11.2.4 The torch, glassware, and aerosol injector tube. The glassware should be clean, with no trace of deposits or signs of melting. Devitrification will occur, but over time in severe cases, cracking will take place. If The torch cracks, the shape of the plasma will change, and the operating characteristics will deteriorate. The torch should be replaced if cracking occurs.

11.2.5 The nebulizer for clogs and the sample capillary tubing for build -up and tube wear. The nebulizer can be removed and placed in a sonicator bath with the wash solution (section 8.4) to clean it.

11.2.6 The radial window is subject to collect sample material if very high solids samples are run. The need to clean the window can be monitored by examination of the standard absolute intensities for selected elements. Follow the procedure in the hardware manual for removal and replacement. Generally, the deposits can be removed with sonication in a nitric acid solution.

11.2.7 If the argon supply is allowed to deplete, the spectrometer will go to standby mode. It is best to turn the spectrometer power off if this occurs. After the argon supply is restored, the instrument will require a warmup, which is conducted in the Diagnostics window. Allow 73 min. for the warmup, and may need to be done twice. It has been observed that even after this warmup, the instrument still requires a day of having argon to become stable.

Note: Perform the warmup as soon as possible after connecting the new argon supply. There are certain hardware functions that do not perform until this software operation is performed.

11.3 If maintenance has been done on the torch compartment, an alignment of the spectrometer viewing optics should be performed. This is done from the Tools option of the menu bar, under Spectrometer Control. For radial view, a 10 mg/L Mn solution is aspirated and the torch viewing position is optimized. For axial view, a 1 mg Mn/L solution is used. This optimization can also be performed as a normal maintenance routine.

11.4 All maintenance must be recorded in the maintenance portion of the standards logbook.

12.0 LIMS ENTRY AND REPORTING

12.1 All LIMS data entry is based on first creating a bench sheet describing the sample preparation. This bench sheet describes the samples prepared, and the digestion quality control samples. The stock spike solutions described in section 8.12 are used here for the matrix spike and blank spike. The analyst must make certain that the preparation date in LIMS matches the actual preparation date. By convention, if the sample preparation proceeds overnight, the date started is used for the LIMS preparation date. Only one blank and blank spike are needed per digestion batch.

12.2 When the data are ready to be entered, the bench sheet is called up into the Data Entry/Review module. All analyses or selected analyses can be included. If only a few analyses are to be entered, data may be entered manually. Otherwise, it may be more practical to use Data Tool.

12.2.1 When performing manual data entry, enter the results in the column **Result** in mg/L. For each result, enter the date of analysis in the column **Analyzed**. This column has a calendar feature as do other date fields in LIMS. If dilutions were necessary for the analysis, enter the dilution in the column **Dilution**. The sample result should be the one measured and not corrected for the dilution factor. Verify that the correct initials are present in the Analyst field and the instrument field.

12.2.2 If all data are entered, click the **Save** button on the top row. After saving, proceed to the Review page by clicking **Query** on the second row. Verify that all conversions to reporting units and dilutions have been calculated correctly. Verify that reporting limits have been correctly applied. Flags may be added at this stage, following the guidance given in SOP GEN005. Before review by the peer, The data may be locked, and the status should be updated to Analyzed.

12.2.3 If Data Tool is to be used, once the batch is called up in Data Entry/Review, click **Export** to create an Excel file in the User Directory. Name this file in a manner that it can be easily associated with that analysis.

12.2.4 A file created in section 9.15.7 (a .prn file) contains the instrument readings for the samples. If multiple measurements for a given sample are present, such as for dilutions, the .prn file can be loaded into a text editor, such as Word Pad, and the sample IDs for the sample readings that are not to be used can be altered so that Data Tool does not recognize them. This altered file must be saved as a .prn file for Data Tool to use it.

12.2.5 Once in Data Tool, click **Browse** for the Element Data Entry Table, and call up the .xls file created in 12.2.3. Click **Browse** for the Instrument Data File, and call up the file created in 9.15.7. If unneeded sample entries remain in the lower left-hand box, click **Clear**. Double-click on the desired .prn file and either **Auto Select** or highlight individual samples and click **Include**.

12.2.6 Once the samples and digestion quality control are selected, click **Done** and it will return to the main Data Tool page. Click **Merge Files**. If either Unmatched Analytes or Unmatched Units appear in red, repair the cross table with the assistance, if necessary, of the Metals Group Leader. Verify that the results in Initial Result are correct, and click **Save**, which will create an Excel file. Name this one differently from the name chosen in 12.2.5 and click **Done**.

12.2.7 Return to the Data Entry/Review module and click **Open**, using the .xls file created in the paragraph above. Verify that all items are correct as in the manual data entry in 12.2.1 and click **Save**. Query the data and proceed as in 12.2.2.

12.2.8 Note that only one analytical line is used per element for Data Tool. If data is to be used from more than one analytical line for different concentration ranges, which is the most common reason, the upload should include the most frequently used line, and edit the others manually. Note which line was used in the narrative.

12.3 LIMS Report Generation

12.3.1 Once all ICP data are entered with the status of Analyzed, prepare a draft report. In LIMS, select Project Management, Reports. Choose the work order and the analyses, and select the report. For atomic absorption analyses, the LIMS analyses are all single element analyses as of this writing. The report chosen will typically be C_Sample_Metals.rpt or CE_Sample_Metals.rpt, unless only a few analytes are reported, in which case C_Analysis_Metals.rpt can be used. If QC is to be omitted from the report, such as with a prep batch shared with ICP, including separate spikes for the two methods, choose Modified Draft, unchecking the quality control samples that were not analyzed. This draft report need not be signed. It is only for the purpose of review.

12.3.2 After the peer reviewer has updated the status of the LIMS entries to Reviewed, the final report may be generated. The mode of generation of the report is the same as above, except that C_Sample_Metals_NoQC.rpt or CE_Sample_Metals_NoQC.rpt would be chosen, and either the Final Report or Modified Final Report is chosen. Again, if only a few analytes are reported, C_Analysis_Metals.rpt can be used. All pages of the report and the transmittal form must be signed and dated.

12.4 For any batch there is a standard set of documents which accompany the data to the evidence files. See the Data Package Requirements Section of the Standard Operating Procedure for the Review of Data Produced in the Analysis for Metals in Environmental Samples, GEN005. The standard set includes:

12.4.1 The original and a copy of the values reported from LIMS for the samples of the batch, including the transmittal form.

12.4.2 An original and a copy of the narrative which describes the analysis and assists the client in evaluating the quality of the data. The requirements for the narrative are described in SOP GEN005.

12.4.3 A copy of the digestion sheet which indicates what samples were digested, who performed the digestion, the date the digestion was performed, the method by which the samples were digested and which shows what other batches, if any, were in the same digestion group.

12.4.4 A copy of the results for all the digestion QC (blanks, duplicates and spikes) of the digestion group. Occasionally, part of a run will be reported because something went wrong with digestion QC in one of the sample groups (ten samples and attendant QC). In this case only the acceptable QC is included in the file. The decision to report only part of a run requires consideration of many factors in the entire run and must be made with consultation among the analyst, group leader and/or the QC coordinator.

12.4.5 A copy of the instrument quality control checks report, including LCB, LCM1, LCM2 and LCMHI. Also include a report of the RLC and SIC solutions. Rarely, part of a run will be reported because something went wrong with instrument QC after one of the sample groups (ten samples and digestion QC). In this case only the acceptable QC is included in the file. The decision to report only part of a run requires consideration of many factors in the entire run and must be made with consultation among the analyst, group leader, and/or the QC coordinator.

12.5 The information listed in 12.4 is submitted to a peer reviewer and other reviewers in a standard order to aid in the data review. The sample values are paper clipped to a QC package that is stapled together and is the same for all samples in the digestion group. The QC package is in the order of digestion preparation sheet, LCB, LCM1, LCM2, LCMHI, RLC, LRB, LFB, duplicate, spike, SICs, and other supporting information (e.g., undigested field blank analysis). Any comments or notes about the QC package or samples is written in a separate narrative, that must be submitted with the data package.

12.6 The original raw data is submitted with the completed data packages, after peer review, to the group leader for final submission. After the final CRL review the raw data is placed with the appropriate sample batch by the data coordinator. The first sheet of the raw data should be initialed and dated by the analyst. Any unusual occurrences during the run should be noted, initialed and dated on the raw data. The original digestion preparation sheet (which is kept in the metals preparation laboratory) will enable the raw data to be found if it is needed.

12.7 The instrument raw data file(s) and all other electronic files related to the sample batch is uploaded to R5CRL. See Protocol for Upload of Inorganic Data to R5CRL, Revision 5 (SOP GEN001).

13.0 REFERENCES

13.1 Federal Register, Vol 49, No. 209, October 26, 1984, pp 43431 - 43436.

13.2 "Methods for Chemical Analysis of Water and Wastes," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati OH 45268, EPA-600/4-79-020, Revised March 1983.

13.3 "ICP WinLab Software Guide," Perkin-Elmer Corporation, 1997.

13.4 "An Atlas of Spectral Interference in ICP Spectroscopy," M. L. Parsons, A. Foster, and D. Anderson (Plenum, New York) 1980.

13.5 Massachusetts Institute of Technology Wavelength Tables G. R. Harrison, ed. (M.I.T. Press, Cambridge, Massachusetts) 1969.

13.6 "Inductively Coupled Plasma-Atomic Emission Spectroscopy," R. K. Winge, V. A. Fassel, V. J. Peterson, and M. A. Floyd (Elsevier Science Publishers, New York) 1985.

13.7 Method 200.7, "Determination of Metals and Trace Elements in water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry" Revision 4.4, EPA/600/R-94/111, May 1994.

13.8 Standard Operating Procedure for the Digestion of Aqueous and Solid Samples by Method 200.2, U.S. Environmental Protection Agency, Region 5 Central Regional Laboratory, 536 South Clark Street (ML-10C) Chicago, Illinois 60605. METALS025.

13.9 Standard Operating Procedure for the Digestion of Aqueous and Solid Samples for Metals Hotplate Digestion, U.S. Environmental Protection Agency, Region 5 Central Regional Laboratory, 536 South Clark Street (ML-10C) Chicago, Illinois 60605. METALS033.

13.10 Standard Operating Procedure for the Review of Data Produced in the Analysis of Metals in Environmental Samples, U.S. Environmental Protection Agency, Region 5 Central Regional Laboratory, 536 South Clark Street (ML-10C) Chicago, Illinois 60605. GEN005.

13.11 Standard Operating Procedure for the Digestion of Aqueous Samples Using Microwave Heating, U.S. Environmental Protection Agency, Region 5 Central Regional Laboratory, 536 South Clark Street (ML-10C) Chicago, Illinois 60605. METALS035.

13.12 Protocol for Upload of Inorganic Data to R5CRL, Revision 5, U.S. Environmental Protection Agency, Region 5 Central Regional Laboratory, 536 South Clark Street (ML-10C) Chicago, Illinois 60605. GEN001.

13.13 Standard Operating Procedure for Central Regional Laboratory (CRL) Analyst Demonstration of Capabilities Including Method Detection Limit (MDL) Studies, Initial Demonstration of Precision and Accuracy and the Preparation, Analysis and Reporting of Performance Evaluation (PE) Study Samples, U.S. Environmental Protection Agency, Region 5 Central Regional Laboratory, 536 South Clark Street (ML- 10C) Chicago, Illinois 60605. GEN012.

13.14 J.K.Taylor, *Quality Assurance of Chemical Measurements*, Lewis Publishers, Inc., Chelsea, Michigan, 1987, Chapter 14.

13.15 Recommendation for Interim Approval of Methods Proposed on October 18. 1995, as Alternate Test Procedures for use in Wastewater Compliance Monitoring, Approval Letter from Maria Gomez-Taylor, 1 May 2002, to allow use of 1994 version of 200.7.